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ON COPPER PEROXIDE

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16. Abstract

The action of hydrogen superoxide on copper salts in alcoholic solutions is studied. The action of hydrogen peroxide on copper hydroxide in alcoholic suspensions, and the action of ethereal hydrogen peroxide on copper hydroxide are discussed. It is concluded that using the procedure proposed to exclude almost entirely the harmful effect of hydrolysis.

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On copper peroxite* **

In a detailed report[1] it was shown at the time that the only way to produce true copper superoxide (copper peroxite or copper peroxidate) is via oxidation of finely distributed copper hydroxide be means of strong hydrogen peroxide in neutral solution; the temperature should be close to 0°. Analysis of the substance obtained generally produced ratios of active oxygen and copper that led to the formula CuO_2. Of course, in most of the cases studied somewhat less oxygen was found, a circumstance that can be attributed to the effect of hydrolysis. Since the production process always took place in aqueous liquid, a hydrolytic equilibrium was established:

$$CuO_2 + 2H_2O \rightleftarrows Cu(OH)_2 + H_2O_2,$$

so that there was always a slight contamination of the peroxide present, in the form of copper hydroxide. From this arises the requirement that the test conditions should be selected in such a way that the influence of water is excluded as much as possible; this could only be achieved by working in alcoholic or ethereal solution at a

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* By L. Moser. Submitted March 21, 1914.

** The use of the expression "copper peroxite" follows a suggestion made by Ebler and Krause, Z. anorg. Chemie 71 (1911), 150, according to which the true salts of hydrogen peroxide are called peroxites, in contrast to peroxidates, which are taken by these researchers to mean only addition compounds of hydrogen peroxide, such as, for example, Tanatar, Z. anorg. Chemie 28 (1901), 255, has described. Since, as a result of this form of expression, the character of peroxide-type substances appears to be immediately defined, the writer has taken up this suggestion and would like at this point to recommend heartily the general introduction of this nomenclature. Naturally, this doesnot affect the designation of untrue superoxides, which, of course, have only one form of constitution.

***Numbers in margin indicate foreign pagination.

low temperature or by proceeding in a similar manner to that used by Bredig and v. Antropoff[2] when producing mercury peroxide, by allowing concentrated perhydrol to act on the metal. The actual impetus to carry out a few experiments using the latter method came from a study of Kastle and Shedd[3] on the breakdown of hydroperoxide by various susbtances; this study contains the remark that, when finely distributed copper and highly concentrated hydrogen peroxide are combined, the copper becomes coated with a black layer that is apparently of a peroxide-like nature and only then does the catalytic /381
breakdown of the hydroperoxide take place. The copper used for these experiments was obtained in a different way: first granulated copper was used, then copper turnings and finally copper in the form of thin copper sheet; in this case the surface of the metal was freed of oxides by brief dipping in nitric acid and then rinsing in water, which made it as reactive as possible. The hydrogen peroxide was used only in 30% solution. In all cases there was a slight development of gas, without any change occurring on the surface of the metal. Even when copper powder was used, at no temperature could the formation of the black coating mentioned by Kastle and Shedd be observed. For this reason, the possibility of producing copper peroxite by this method was ruled out. On the other hand, the following three methods of producing copper peroxite were accompanied by success.

a) Action of hydrogen superoxide on copper salts in alcoholic solution

An alcoholic 2-norm. $CuCl_2$ solution was used that contained 42.62 g $CuCl_2 . 2$ aq per liter and always 30% Merck perhydrol. 20 ccm of this solution were cooled in a wide test tube to -40 to 50°, by means of solid carbon dioxide and acetone, then 10 ccm of hydrogen peroxide were added and finally some alcoholic caustic potash solution was added, while stirring constantly. The mixture immediately turned brownish-black and copper peroxite was formed. Because of the low temperature, it is important to make sure that the components are thoroughly mixed, because otherwise lumps of copper hydroxide may escape the reaction with the hydrogen peroxide. At this temperature no gas formation and thus no catalytic decomposition were observed. The dark brown colored product was liberated from the solution by

means of suction using a Buechner funnel and was immediately flushed with cold alcohol (-50°) and ether until the filtrate did not produce any hydrogen peroxide reaction with titanium sulfate any more. It should be emphasized that during this operation there was no perceptible production of oxygen, while this always occurred in aqueous solution.

The analysis was carried out again using the "combined" method, which has been described in an earlier report[4]. Thus the peroxite /382
was first mixed with diluted sulfuric acid (this was 1-norm.) at room temperature in the azotometer, the oxygen formed was measured and then the hydrogen peroxide that formed was titrated with potassium permanganate solution. The amount of oxygen formed by the acid depends, as will be shown later, largely on the reaction temperature and the concentration of the acid; there is no doubt that the primary product of the decomposition process is only hydrogen peroxide, but the latter undergoes partial decomposition in oxygen and water, which is temperature-related, so that the level of oxygen found after direct titration is always somewhat too low. The titrated solution was then electrolyzed, with a few drops of nitric acid added to measure the copper, and the ratio Cu : O act. is determined from the figures. It should also be noted that the following three analyses were carried out <u>immediately</u> after flushing, as the moist product loses part of the oxygen after a while.

1 Versuch 1. 1 ccm $KMnO_4$ . . . 0.001723 g O
2.9 ccm O $t = 16.0°$, $B = 748$ mm
31.2 ccm $KMnO_4$
2 Gefunden: 0.00377 g O (gasf.)[5] + 0.02688 g O = 0.03065 g O
0.1248 g Cu
Cu : O = 1.02 : 1
3 Versuch 2. 4.2 ccm O $t = 18°$, $B = 750$ mm
42.1 ccm $KMnO_4$
2 Gefunden: 0.00543 g O (gasf.)[5] + 0.03635 g O = 0.04178 g O
0.1860 g Cu
Cu : O = 1.12 : 1
4 Versuch 3. 3.6 ccm O $t = 18°$, $B = 750$ mm
35.9 ccm $KMnO_4$
2 Gefunden: 0.00465 g O (gasf.)[5] + 0.03067 g O = 0.03532 g O
0.1488 g Cu
Cu : O = 1.06 : 1

<u>Key</u>:

1 experiment 1
2 found
3 experiment 2
4 experiment 3
5 gaseous

b) Action of hydrogen peroxide on copper hydroxide in alcoholic suspension

Copper hydroxide was produced at a cold temperature by means of precipitation of a copper chloride solution using caustic potash solution; somewhat less of the latter was added than the theoretically required amount, so that the flushing would take place more readily. After decanting 7 times with cold water, the precipitate was dried slightly and then triturated with alcohol (96%). The alcoholic suspension was cooled to -40° and mixed with 30% hydrogen peroxide. At this temperature the reaction rate between the two substances is very slow; not until the tube was taken out of the cold mixture several times for a short time did the mass turn a brownish-black color. It was not possible to discern the formation of oxygen during these operations. The precipitate was then sucked through a cooled filter and flushed with alcohol at -40° until no further hydrogen peroxide was detectable in the filtrate. The measurement of the ratio of Cu : O act. was done immediately after the product was formed. /383

1 Versuch 4. 1.3 ccm O $t = 17°$, $B = 751$ mm
52.4 ccm $KMnO_4$
2 Gefunden: 0.00169 g O (gasf.)[5] + 0.04514 g O = 0.04683 g O
0.2009 g Cu
Cu : O = 1.08 : 1

3 Versuch 5. 2.6 ccm O $t = 17°$, $B = 751$ mm
41.2 ccm $KMnO_4$
2 Gefunden: 0.00338 g O (gasf.)[5] + 0.03549 g O = 0.03887 g O
0.1547 g Cu
Cu : O = 1.00 : 1

4 Versuch 6. 3.8 ccm O $t = 18°$, $B = 746$ mm
43.4 ccm $KMnO_4$
2 Gefunden: 0.00489 g O (gasf.)[5] + 0.03739 g O = 0.04228 g O
0.1781 g Cu
Cu : O = 1.06 : 1

Key: 1 experiment 4; 2 found; 3 experiment 5; 4 experiment 6; 5 gaseous.

c) Action of ethereal hydrogen peroxide on copper hydroxide

The production of peroxite in this manner offered the possibility of allowing the reagents to act on each other in a truly waterless state and also of excluding the presence of hydroxyl ions. The ethereal solution of hydrogen peroxide wasproduced by agitating Merck perhydrol with ether in an agitation funnel; to 20 g of the former /384 were added 70 ccm of the latter. The ethereal solution formed in this way contained about 1.5 g H_2O_2. The blue copper hydroxide was also dried completely , then finely triturated and finally "sifted", so that it became an extremely fine powder. The copper peroxite was produced by allowing the ehtereal solution of H_2O_2 to act in several portions on the copper hydroxide contained in a glass trituration dish, stirring all the while and compressing the reaction mixture with a pestle; the temperature was kept close to zero. At the beginning of the reaction there was violent gas formation, but this ceased after a few minutes; its origin could undoubtedly be attributed to the separation of the water from the copper hydroxide; this process corresponds to the following scheme:

$$Cu\begin{matrix}OH\\OH\end{matrix} + \begin{matrix}H-O\\H-O\end{matrix} \rightleftharpoons Cu\begin{matrix}O\\O\end{matrix}\cdot H_2O + H_2O; \qquad (1)$$

$$CuO_2 + H_2O \rightleftharpoons Cu(OH)_2 + {}^1/_2O_2. \qquad (2)$$

One molecule of water is thus immediately bound as crystal water, hwile the other dsitributes itself in the ether. It is understandable that the disadvantageous effects of the water are not very noticeable here, as there is such a small amount present. In fact it was always possible to observe that the oxygen release ceased completely after a few minutes. After stirring for 10 min, during which the reaction mass was well stirred with the pestle, the mixture was filtered with suction and flushed with waterless ether until the hydrogen peroxide reaction disappeared; then the product was liberated of the final traces of ether in the vaccum exsiccator and immediately analyzed:

1 Versuch 7. 5.1 ccm O $t = 17°$, $B = 747$ mm
33.68 ccm $KMnO_4$
2 Gefunden: 0.0066 g O (gasf.) + 0.0295 g O = 0.0361 g O
0.1492 g Cu
Cu : O = 1.04 : 1.
3 Versuch 8. 3.6 ccm O $t = 10°$, $B = 755$ mm
32.60 ccm $KMnO_4$
2 Gefunden: 0.0046 g O (gasf.) + 0.0562 g O = 0.0608 g O
0.2587 g Cu
Cu : O = 1.07 : 1.

Key: 1 experiment 7; 2 found; 3 experiment 8; 4 gaseous.

These three methods are therefore suitable for producing copper /385
peroxite, since, as a result of working in alcoholic or ethereal solution, the hydrolysis of the peroxite formed and its catalytic decomposition are very slight. The last method described will mainly be advantageous to use when one wishes to avoid working at low temperatures. If one compares the ratios found with those from an earlier report[5], then one finds that with the new method the substance is produced in more pure form; while earlier the method produced out of 14 measurements the value Cu : O = 1.15 : 1, the new method now produces from 8 measurements 1.05 : 1. The appearance and the properties of the peroxite are the same and what was said earlier applies to them both.

It has been shown that hydrogen peroxide and small amounts of oxygen are formed as a result of the action of diluted acids on copper peroxite. It appears that the formation of oxygen is the result of the partial catalytic decomposition of the hydrogen peroxide formed. It has been shown that, by treating the peroxite with very diluted acid at a temperature close to zero, the catalysis under these conditions produced only a very small yield. However, it should be noted that this observation applies only to peroxite that is as little decomposed as possible, i.e. freshly produced peroxite, since a partially decomposed product always forms large amounts of oxygen with diluted acids, probably as a result of its copper oxide content. It is likely that in this case the copper oxide already formed has

a catalyzing effect on the hydrogen peroxide and thus large amounts of oxygen are split off. The following experiments, 9 and 10, demonstrate that freshly prepared copper peroxide produces more oxygen with a stronger acid at a higher temeprature than with a weaker acid at a lower temperature.

Experiment 9. Decomposition was carried out using 1-norm. H_2SO_4 at 17°.

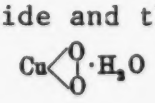
2.7 ccm O $t = 17°$, $B = 753$ mm
35.20 ccm $KMnO_4$
2 Gefunden:
0.00352 g O (gasf.)$_3$ + 0.03027 g O (aus H_2O_2)$_1$ = 0.03379 g O.
0.1383 g Cu
Cu : O = 1.03 : 1; O (gasf.)$_3$: O (aus H_2O_2)$_1$ = 1 : 8.65

6 / 1. e.

Experiment 10. A second portion of the same product was dissolved 7° using 1/10 norm. H_2SO_4 /386

0.22 ccm O $t = 7°$, $B = 755$ mm
41.20 ccm $KMnO_4$
2 Gefunden:
0.00027 g O (gasf.)$_3$ + 0.03549 g O (aus H_2O_2)$_1$ = 0.03576 g O
0.1493 g Cu
Cu : O = 1.05 : 1; O (gasf.)$_3$: O (aus H_2O_2)$_1$ = 1 : 136.5.

Key: 1 from; 2 found; 3 gaseous.

Thus there is no doubt that copper peroxite can be considered a salt of hydrogen peroxide and that thus it has the constitution of the true peroxides  . It is a relatively unstable substance

that at room temperature already has a tendency to turn into copper oxide while constantly giving off oxygen. When heated for a moment it suddenly loses its active oxygen; the substance is transformed to copper oxide in a process that produces fire and disintegration. This phenomenon can be observed very clearly if one stirs a small

amount of dried peroxite with a warm glass rod or with one drop of conc. sulfuric acid; a harmless explosion occurs which is accompanied by the obvious development of light.

Other experiments to produce copper peroxite

Since, according to the last method described, hydrolysis still takes place as a result of the reaction mechanism, even if only to a limited extent, we wanted to try to exclude this completely by means of a suitable process. The production of zinc peroxide by E. Ebler and R. Krause[6], by means of the action of zinc alkyl on ethereal hydrogen peroxide, with all moisture excluded, provided a signpost in this direction. Accordingly a coppler alkyl came under consideration as the raw material; this had not so far been successfully produced[7]. An attempt was made to extend the Grignard rection to copper salts. For this it is necessary that the copper salt be soluble in waterless ether; this requirement is not met by normal salts and it was only after a long search that we found an organic salt that possessed this property to a sufficient extent: this substance is oleic acid copper. /387 The magnesium halogen alkyl compound $MgBrC_2H_5$ dissolved in absolute ether was allowed to act on this salt. Despite all kinds of changes inthe test conditions, we did not succeed in obtaining copper alkyl. Even the modification suggested by Tschelinzeff[8], using benzene instead of ether and adding a few drops of dimethyl aniline as a catalyst, did not bring success. Copper bromide was also combined with magnesium halogen alkyl in ethereal solution, which produced a violent reaction. The ethereal layer was tested for copper after being heated for 2 hours in a water bath (reflux condenser), but this experiment also had a negative result.

Once we saw that this path was not going to lead to success, we tried to use the otherwise highly reactive copper acetylene Cu_2C_2; this was produced according to the information provided by Soederbaum[9], by introducing acetylene into an ammoniacal copper sulfate solution, which was mixed with so much sulfuric acid that it became completely colorless. This was based on the theory that the reaction in ethereal solution would take place more or less according to the following scheme:

$$Cu_2C_2 + 2H_2O_2 \longrightarrow 2CuO_2 + C_2H_2.$$

When the ethereal H_2O_2 solution was allowed to flow in there was slight hissing and formation of gas; a small amount of the copper acetylene disintegrated into copper and carbon, while the main portion was not changed. The explosion samples with the residue tested positive and H_2O_2 could not be detected after dissolving in acid.

Finally, an attempt was made, based on the now generally recognized theory of auto-oxidation processes of Engler, according to which oxygen is primarily always added as a whole molecule to a molar oxide, to oxidize colloidal copper, which according to the information given by The Svedberg[10] had been obtained as isobutyl alcosol by means of cathodic disintegration, using pure oxygen or ozone. After being briefly introduced into the colloidal copper solution of these gasses, a brownish-black substance was precipitated that was hard to dissolve in diluted acids and was identified as copper oxide.

Summary

/388

1. Copper peroxite with the formula $CuO_2.H_2O$ is produced as a result of the action of hydrogen peroxide on copper salts in alcoholic suspension at low temperatures.
2. Copper peroxite is also produced as a result of the action of etheral hydrogen peroxide on finely triturated blue copper hydroxide; the temeprature only has to be kept close to zero.
3. It has been shown that it is possible, using this procedure, to exclude almost entirely the harmful effect of hydrolysis; the measurement of the Cu : O act. ration produced on average the ratio 1.05 : 1, proof that the resulting product was of great purity. The true character of the peroxite is backed up by the circumstance that it is possible, at a temperature close to zero and using very diluted acid, to split off almost all active oxygen in the form of H_2O_2.
4. Finally an attempt was made to carry out the production of this peroxite by various other methods, without success.

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10 The Svedberg: Ber. 38 (1905), 3620; 39 (1906), 1712.